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Reimer - The Addition Reaction of Sulphuric Acids
Macdonald - A New Class of Disulphones

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MONOGRAPH SERIES, Vol. I, No. 2

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ANNOUNCEMENT

The Bryn Mawr College Monographs are issued in two series; the first, the **Monograph Series**, containing articles that appear here for the first time; the second, the **Reprint Series**, containing reprints of articles that have appeared in other journals.

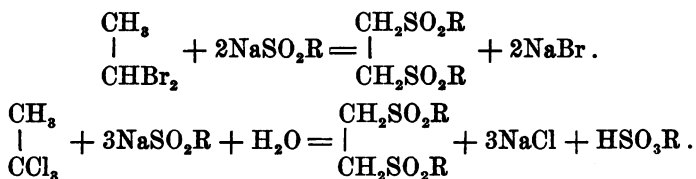
It is proposed to publish these monographs in separate numbers at irregular intervals as material is accumulated. The numbers will be combined into volumes of about 500 pages.

The monographs are edited by a committee of the Faculty of Bryn Mawr College, consisting at present of President M. Carey Thomas, ex-officio, Professor Thomas Hunt Morgan (chairman), Professor Charlotte Angas Scott, and Professor Charles McClean Andrews.

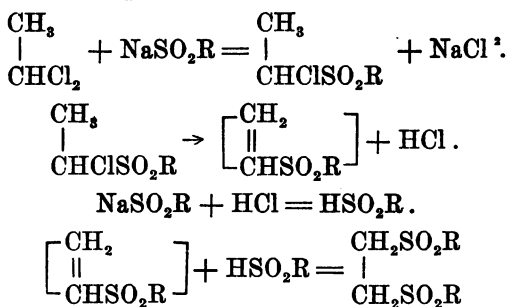
14

THE ADDITION REACTIONS OF SULPHINIC ACIDS.

The study of the sulphinic acids and their salts has led to the discovery of certain peculiar reactions for which no satisfactory explanation has been offered. Otto¹ found, for example, that unsymmetrical di- or tri-halogen substituted aliphatic hydrocarbons yield symmetrical di-sulphones when treated with a sodium sulphinate:



These reactions Otto explained by assuming molecular rearrangement, an assumption for which there is no experimental evidence and which is improbable. An interpretation not involving molecular rearrangement is possible by assuming the formation of an intermediate unsaturated compound, which subsequently combines with the sulphinic acid to form the final product:

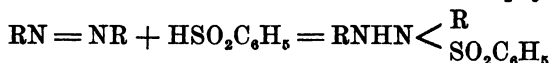
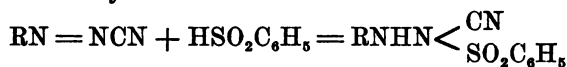


¹ J. prakt. Chem., [2] 40, 505.

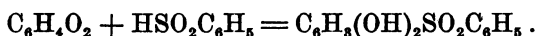
² Otto: J. prakt. Chem. [2] 40, 505.

This mechanism is based on the assumption that sulphinic acids are capable of combining directly with unsaturated compounds and that this combination takes place in a definite way.

But few cases of addition reactions of sulphinic acids are known. Hantzsch and Glogauer³ found that benzene sulphinic acid combines with azo and diazo compounds to form sulphone hydrazo compounds and hydrazones:



Hinsberg⁴ found that sulphinic acids add to quinone and to substances having a quinoid structure:



No case of direct addition of a sulphinic acid to a double linkage between carbon atoms has been described. In view of the analogy between sulphinic acids and acid sulphites, it seemed probable, however, that these acids would combine, as do the sulphites, with a number of unsaturated compounds. The object of this investigation was to determine with what classes of unsaturated compounds sulphinic acids combine, the conditions under which such combination takes place, the structure of the resulting compounds and the extent to which these addition reactions account for the abnormal reactions before mentioned.

The reactions of sulphinic acids with unsaturated acids were studied first, because it seemed improbable that sulphinic acids would combine with the carbonyl group in view of the fact that reactions which would be expected to give α , oxysulphones give only products of decomposition of these substances.⁵ In the course of the work, the reactions with cinnamic aldehyde were investigated and it was found that, in this case, the sulphinic acid adds to the aldehyde group. The work was, therefore, extended to other aldehydes.

³ Ber. d. chem. Ges., **30**, 2548.

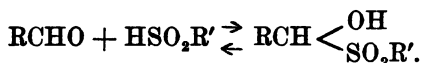
⁴ Ber. d. chem. Ges., **27**, 3259.

⁵ Fromm: Ann. Chem., (Liebig) **253**, 135,

The experiments described include the addition reactions of sulphinic acids with saturated and unsaturated aldehydes, unsaturated acids, and saturated and unsaturated ketones.

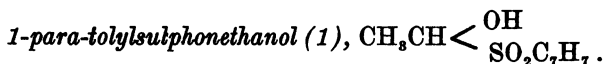
I. ADDITION OF PARA-TOLUENE SULPHINIC ACID TO SATURATED ALDEHYDES.

While this work was in progress, a paper by Meyer* on the reactions of para-toluene sulphinic acid appeared. Meyer found that para-toluene sulphinic acid combined with formaldehyde but not with acetaldehyde nor benzaldehyde. The following experiments show, however, that the combination of toluene sulphinic acid with aldehydes is a general reaction. In many cases it is extremely difficult to isolate the addition-products. This is explained by the fact that the reaction is a reversible one, taking place according to the equation:



The products can be isolated only under particular conditions.

1. Addition to acetaldehyde:



When p-toluene sulphinic acid is treated with acetaldehyde there is an evolution of heat showing that a reaction takes place. In order to isolate the product it was found necessary to carry on the reaction in ethereal solution. A considerable excess of the aldehyde was added to an ethereal solution of the sulphinic acid and the mixture boiled for half an hour. The solution was then cooled with ice-water and ligroin added slowly. The addition-product separated in thick white plates. It was dissolved several times in ether to which a few drops of acetaldehyde were added and reprecipitated with ligroin. The substance was then filtered, dried rapidly in a current of air and analyzed at once.

*J. prakt. Chem., [2] 68; 167.

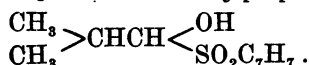
- I. 0.2291 gr. subs. gave 0.4531 gr. CO₂ and 0.1261 gr. H₂O .
 II. 0.2254 gr. subs. gave 0.4442 gr. CO₂ .
 III. 0.2089 gr. subs. gave 0.2692 gr. BaSO₄ .

	Calculated for C ₉ H ₁₁ SO ₃	I.	Found. II.	III.
C	54.00	53.94	53.73	
H	6.00	6.11		
S	16.00			16.5

The compound separates in thick plates which may be kept for some time in solution in ether and ligroin containing a little acet-aldehyde. It is extremely unstable in the air, giving up the aldehyde. For this reason it does not melt sharply. It begins to soften at 52° and is liquid at 72°.

2. *Addition of para-toluene sulphinic acid to isobutyl aldehyde:*

1-*para*-tolylsulphon-3-methylpropanol (1),



Five grams of sulphinic acid were dissolved in ether and added to an ethereal solution of three grams of isobutyl aldehyde. The solution was boiled and cooled. The product of the reaction separated out on addition of ligroin. It was dissolved again in ether, reprecipitated with ligroin, washed with ether and dried on a porcelain plate.

0.2020 gr. subs. gave 0.4277 gr. CO₂ and 0.1290 gr. H₂O .

	Calculated for C ₁₁ H ₁₆ SO ₃ .	Found.
C	57.90	57.67
H	7.02	7.09

The substance crystallizes from ether in colorless needles, from ether and ligroin in thick plates. It melts at 72°-73°. It is unstable in the air.

3. *Addition of para-toluene sulphinic acid to heptioic aldehyde:*

1-*para*-tolylsulphon heptanol (1), CH₃(CH₂)₅CH < $\begin{array}{c} \text{OH} \\ \text{SO}_2\text{C}_6\text{H}_7 \end{array}$

Ethereal solutions of the two substances in molecular proportions were brought together, boiled and cooled. The product

separated on addition of ligroin. It is less soluble in ether than the substances previously described, hence it was possible to purify it by dissolving it in boiling absolute ether and cooling the solution in ice-water.

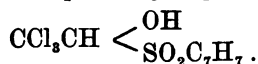
- I. 0.1932 gr. subs. gave 0.4361 gr. CO_2 and 0.1386 gr H_2O .
 II. 0.2224 gr. subs. gave 0.5020 gr. CO_2 and 0.1608 gr. H_2O .

	Calculated for $\text{C}_{14}\text{H}_{11}\text{SO}_3$.	Found.	
		I.	II.
C	62.22	61.56	61.55
H	8.15	7.97	8.03

The substance crystallizes in fine white needles, melting at 72° . It is insoluble in water and ligroin, readily soluble in ether, alcohol, acetone, benzene and chloroform. It is unstable, losing aldehyde on exposure to the air.

4. *Addition of para-toluene sulphinic acid to chloral:*

2, 2, 2-trichlor-1-para-tolylsulphonethanol (1),



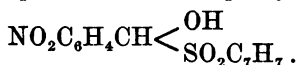
Ethereal solutions of the two substances in molecular proportions were brought together and heated as in the other cases. A dense white crystalline precipitate was formed on the addition of ligroin. The compound was extremely difficult to purify and was not further investigated.

5. *Addition of para-toluene sulphinic acid to benzaldehyde:*

When the sulphinic acid was treated with benzaldehyde there was no evidence of a reaction. If ethereal solutions of the two substances were brought together and allowed to stand at room temperature no product separated. If this ethereal solution was heated as in the other cases and ligroin added an addition-product separated out. This product was exceedingly unstable and could not be obtained in condition pure enough for analysis.

6. *Addition of para-toluene sulphinic acid to meta-nitro-benzaldehyde:*

1-para-tolylsulphon-1-meta-nitro-phenylmethanol (1),



Ethereal solutions of the two substances in molecular proportions were brought together and heated on the water-bath. After a few minutes a white solid separated. It was washed with ether, dried by suction and burned.

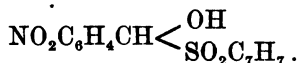
0.2860 gr. subs. gave 0.5738 gr. CO₂ and 0.1139 gr. H₂O .

	Calculated for C ₁₁ H ₁₁ NSO ₃ .	Found.
C	54.72	54.71
H	4.23	4.43

The substance crystallizes in fine white needles, melting to a yellow liquid at 101°. It is readily soluble in alcohol and acetone, slightly soluble in ether. It is stable in the air. It is decomposed by boiling water in which the sulphinic acid dissolves, leaving some of the aldehyde behind. Sodium carbonate solution decomposes it slowly in the cold, rapidly on heating.

7. *Addition of para-toluene sulphinic acid to p-nitro-benzaldehyde:*

1-para-tolylsulphon-1-para-nitro-phenylmethanol (1),



The compound was made by the same method as that from m-nitro-benzaldehyde. After its separation from the ethereal solution it was washed several times with ether and then crystallized from acetone.

0.2028 gr. subs. gave 0.4070 gr. CO₂ and 0.0786 gr. H₂O .

	Calculated for C ₁₄ H ₁₁ NSO ₃ .	Found.
C	54.72	54.73
H	4.23	4.08

The substance separates from ether in very fine, yellowish needles. It crystallizes from acetone in larger needles of a creamy-yellow color. It melts at 116°. It is soluble in alcohol and acetone, slightly soluble in ether, insoluble in ligroin and water.

By the action of acetic anhydride upon tolyl-sulphoncarbinole, CH₃C₆H₄SO₂CH.OH, Meyer¹ obtained a compound which he considers an acetyl derivative of the alcohol, CH₃C₆H₄SO₂CH₂OCOCH₃.

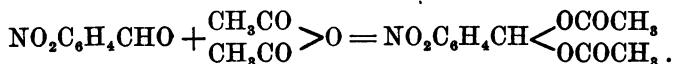
¹J. prakt. Chem., [2] 63; 167.

As the product obtained by the action of para-toluene sulphinic acid on para-nitro-benzaldehyde is stable, it would be expected that an analogous reaction would take place and an acetal be formed. Para-tolyl-sulphone para-nitro-carbinole reacts with acetic anhydride in the cold. The sulphone carbinole dissolved completely in the anhydride. The solution was then evaporated and beautiful needle-shaped crystals separated. An analysis gave the following results:

0.1977 gr. subs. gave 0.8771 gr. CO_2 and 0.0784 gr. H_2O .

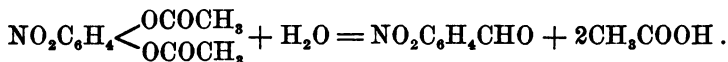
	Calculated for $\text{NO}_2\text{C}_6\text{H}_4\text{CH} \begin{smallmatrix} \text{OCOCH}_3 \\ \text{SO}_2\text{C}_6\text{H}_4 \end{smallmatrix}$	Found.	Calculated for $\text{NO}_2\text{C}_6\text{H}_4\text{CH} \begin{smallmatrix} \text{OCOCH}_3 \\ \text{OCOCH}_3 \end{smallmatrix}$
C	55.01	52.01	52.17
H	4.29	4.40	4.35

The analysis indicates that this substance is not the acetyl derivative of the sulphone carbinole but is the product of addition of a molecule of acetic anhydride to one of p-nitro-benzaldehyde, according to the following equation:



When boiled with concentrated hydrochloric acid for some time the substance slowly dissolves, the liquid becomes slightly yellow and a yellowish oil separates. If the solution be boiled until the oil which separates at first redissolves and then allowed to cool slowly, long, brittle, pale-yellow needles separate which melt at 105° - 106° . This is para-nitro-benzaldehyde.

If the compound be boiled with caustic potash for about twenty minutes, the solution evaporated and sulphuric acid added, there is a strong odor of acetic acid. These reactions, with the analysis, prove that the substance is a diacetyl derivative of para-nitro-benzaldehyde. It is broken down into its components by the action of acids and alkalis:



The compound crystallizes from alcohol in white needles. It melts at 126.5° .

When the filtrate, from which the diacetyl derivative separated, is concentrated by evaporation crystals of p-toluene di-sulphoxide separate. This proves that the sulphinic acid was split off from the addition-product by the action of acetic anhydride.

The ease with which the formation of the diacetyl derivative of the aldehyde takes place is remarkable since, while the acetal is formed from the oxysulphone in the cold, none was obtained by heating the aldehyde directly with acetic anhydride. The two substances were heated for some time in a sealed tube to 150°. No diacetyl derivative was formed.

Meyer* found that tolylsulphone carbinol, when treated with aniline in ethereal solution, formed a compound which he considers the corresponding anilide: $C_6H_4(CH_2)_2SO_2CH_2NHC_6H_5$. In order to test the action of aniline on the addition-product of toluene sulphinic acid with para-nitro-benzaldehyde, a small quantity of the latter substance was added to a hot solution of aniline in ether. It dissolved at once. Almost immediately fine, white, needle-shaped crystals separated from the hot solution, and still more separated on cooling. The substance was very soluble in water and alcohol, insoluble in ether. It melted at 121°-122°. It was found to be identical with the substance formed by treating toluene sulphinic acid in ether solution with aniline and is, therefore, the aniline salt of sulphinic acid formed by the decomposition of the addition-product and the subsequent action of the aniline on the sulphinic acid thus set free.

II. ADDITION TO AN UNSATURATED ALDEHYDE.

1. *Addition of para-toluene sulphinic acid to cinnamyl aldehyde:*

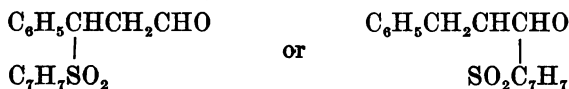
Equivalent quantities of cinnamyl aldehyde and sulphinic acid in alcoholic solution were boiled for two hours on the water-bath. On cooling, a solid separated in yellow globules. It was recrystallized from a mixture of benzene and ligroin in proportions 1:3 and dried in a current of air. The analysis showed that it was the product of addition of one molecule of sulphinic acid to one of aldehyde.

*J. prakt. Chem., [2] 63, 167.

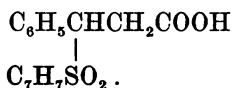
0.2285 gr. subs. gave 0.5580 gr. CO_2 and 0.1101 gr. H_2O .

	Calculated for $\text{C}_{11}\text{H}_{11}\text{SO}_2$	Found.
C	66.66	66.59
H	5.55	5.35

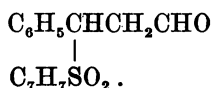
The substance separates in white globules from alcohol. It is soluble in ether and benzene, insoluble in ligroin and water. It melts at 78° . A small quantity of this substance in ethereal solution was shaken with an aqueous solution of acid potassium sulphite. A crystalline compound separated out at once, from which dilute alkalis regenerated the original substance, indicating that the addition of the sulphinic acid to the cinnamic aldehyde had taken place at the doubly linked carbon atoms. For such a substance there are two possible formulas:



In order to determine the structure the aldehyde was oxidized by heating for some time with dilute nitric acid (1:3) on the water-bath. An acid separated from the solution on cooling in very fine white needles, melting at 196° - 197° . The same acid had previously been obtained by the addition of para-toluene sulphinic acid to cinnamic acid. It will be shown later that this acid has the formula:



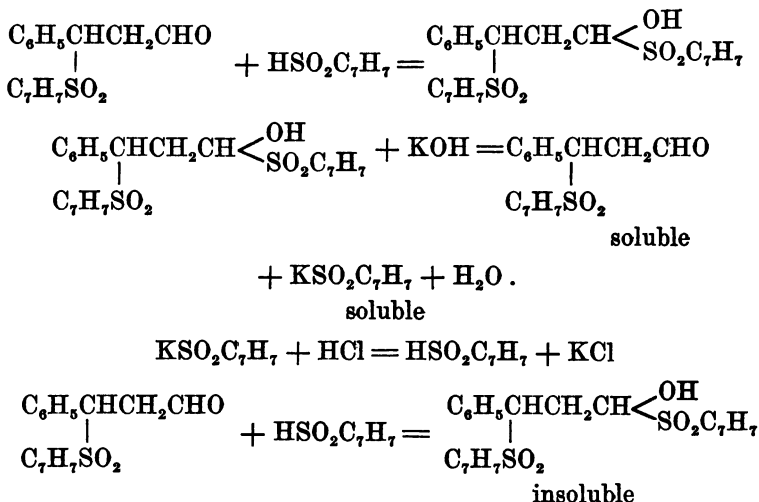
The aldehyde addition-product is, therefore, β -para-tolylsulphone hydrocinnamic aldehyde,



In ethereal solution this sulphone aldehyde combines with more sulphinic acid. One equivalent of sulphone aldehyde was added to one of sulphinic acid in ethereal solution. A copious, flocculent white precipitate formed in the cold. This substance is insoluble in ether and cold water. It is soluble in benzene, alcohol and hot

water, separating from water as a fluffy white solid. When first precipitated it melts, with decomposition, at 114° - 120° . After being repeatedly washed with ether it melts at about 126° . It is unstable, losing sulphinic acid easily and, for this reason, could not be obtained pure enough for analysis. Repeated crystallizations from water and extractions with ether do not serve to purify it.

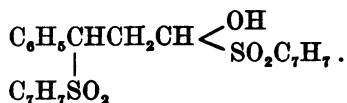
This substance was found to be soluble in alkalies and to be reprecipitated by acids. The only explanation for this seems to be that the second molecule of sulphinic acid had reacted with the sulphone aldehyde to form a di-addition-product. This second molecule would be attached to the aldehyde group and, therefore, less firmly held than the first, so that it could be split off by alkalies to form a sulphinate, leaving the main addition-product in solution. On addition of acid the sulphinate would become free sulphinic acid, which would again add to the aldehyde group to form the insoluble di-addition-product.



In order to prove this, exactly two equivalents of sulphinic acid were added to one of cinnamic aldehyde in ether. The same flocculent white substance separated. After allowing the solution

to stand for some time it was heated on the water-bath for one hour. The solid was then filtered off, more cinnamic aldehyde added to the filtrate and the latter heated. No further precipitation took place, showing that all the sulphinic acid had been used up in the first reaction and that two molecules of sulphinic acid had, therefore, united with one of cinnamic aldehyde.

The compound was washed repeatedly with ether, then dissolved in a strong solution of sodium carbonate and the resulting solution extracted several times with ether. The ether extract was concentrated by evaporation and ligroin added. A solid separated out in yellow globules, which proved to be the mono-sulphone addition-product. The compound is, therefore, the di-addition-product:



The molecule of sulphinic acid attached to the aldehyde group was split off in alkaline solution and the mono-sulphone thus freed was extracted from the solution by ether.

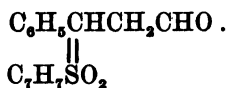
The di-sulphone is also oxidized by nitric acid to β , β , p-tolyl sulphone phenylpropionic acid, showing that the second molecule of sulphinic acid is split off by acids. The sulphone aldehyde is then oxidized as before.

The di-sulphone is always formed when the sulphinic acid and cinnamic aldehyde are brought together in the absence of a solvent or in aqueous or ethereal solution. In alcohol it is formed only when two molecules of sulphinic acid are added to one of aldehyde. The difference in the course of the reaction in alcohol and in other solvents is due to the fact that both the mono- and di-addition-products are extremely soluble. In ethereal solution the difficultly soluble di-addition-product is formed at once. In alcoholic solution, if one molecule of sulphinic acid is present, it probably first combines with the aldehyde group to form



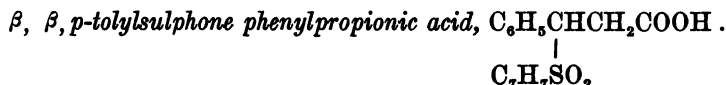
On heating the solution this undergoes a rearrangement, analogous

to that of the corresponding acid sulphite addition-product* to form



III. ADDITION TO UNSATURATED ACIDS.

1. Addition of *para*-toluene sulphinic acid to cinnamic acid:



Para-toluene sulphinic acid and cinnamic acid in molecular proportions were boiled in water in a flask connected with reflux condenser for several days. Both acids melted down to an oil under water. After boiling for a few hours part of this oil had solidified and, after three days, none was left. The liquid contained a hard, yellowish solid and plate-like crystals with a pearly lustre. The solid was filtered off and treated with a hot solution of sodium carbonate in which nearly all of it dissolved. The solution was filtered while still hot. On cooling, a sodium salt separated out as a heavy white precipitate. This was dried on a porcelain plate, extracted twice with boiling ether to rid it of impurities, and dissolved in water. From this solution an acid was precipitated by the addition of dilute sulphuric acid. It was crystallized several times from large quantities of hot water and analyzed.

0.1608 gr. subs. gave 0.3719 gr. CO_2 and 0.0725 gr. H_2O .

$$\% \text{ C} = 63.08$$

$$\% \text{ H} = 5.02$$

These results agree with the calculated percentages of carbon and hydrogen in a compound formed by the direct addition of one molecule of *para*-toluene sulphinic acid to one of cinnamic acid:

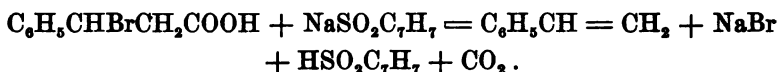
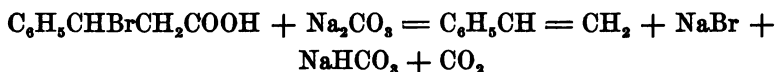
	Calculated for $\text{C}_{14}\text{H}_{18}\text{SO}_4$	Found.
C	63.15	63.08
H	5.26	5.02

* Heusler: Ber. d. chem. Ges., 24, 1805.

For such an acid there are two possible formulas, as the sulphone group may be in the α or the β position:



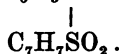
To determine the structure of this acid the following method was adopted. Fittig found that hydrobromic acid combines with cinnamic acid to form β, β , bromphenylpropionic acid, $\text{C}_6\text{H}_5\text{CHBrCH}_2\text{COOH}$. This acid, when treated with sodium sulphinate, should give a β , sulphone propionic acid, $\text{C}_6\text{H}_5\text{CH}(\text{SO}_2\text{R})\text{CH}_2\text{COOH}$. In the course of this reaction, however, carbon dioxide was split off and styrene formed, the sodium sulphinate having the same action on the acid as sodium carbonate:



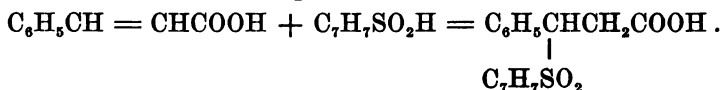
To guard against this action the methyl ester of the acid was used in place of the acid itself.

Cinnamic acid was dissolved in absolute methyl alcohol and the solution saturated with hydrobromic acid. The methyl ester of β brom cinnamic acid crystallized out on cooling. It was treated, in methyl alcohol solution, with an equivalent quantity of sodium toluene sulphinate and boiled until sodium bromide no longer precipitated. The sodium bromide was filtered off, the alcoholic solution evaporated to dryness on the water-bath and the residue crystallized from ether. The ester crystallized in fine white needles. When boiled with dilute hydrochloric acid the ester was saponified to the corresponding acid. This acid is identical with the one formed by the addition of p-toluene sulphinic acid to cinnamic acid. Since the ester was obtained by replacing the bromine atom in β brom cinnamic acid with the para-toluene sulphone group, it follows that the acid is β, β , p-tolylsulphone phenyl propionic acid and the structure of the acid obtained by

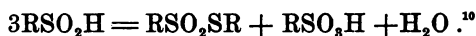
the addition of p-toluene sulphinic acid to cinnamic acid is represented by the formula, $\text{C}_6\text{H}_5\text{CHCH}_2\text{COOH}$



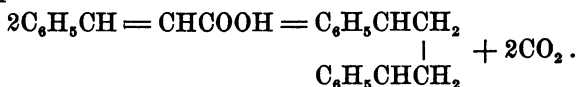
The main reaction takes place as follows:



The reaction is not a perfectly clean one. A small quantity of a substance not soluble in hot sodium carbonate was obtained. This was filtered off and by repeated crystallizations from alcohol was separated into para-tolyldisulphoxide and distyrene. Disulphoxides are always formed, when sulphinic acids are heated with water, as is shown by the equation:



The small quantity of distyrene was formed by the decomposition of part of the cinnamic acid:



It was found, later, that a better method for preparing the addition-product was to heat the sulphinic and cinnamic acids under pressure. Ten grams of cinnamic acid, 10.5 grams of sulphinic acid and about 35 cc. of water were heated in a closed tube for about fifteen hours at 110° . The solid separated out as before but it was much freer from by-products.

β, β , *p*-tolylsulphonephenylpropionic acid is insoluble in cold water. It dissolves very slowly in large quantities of hot water from which it separates on cooling as a fluffy white solid, consisting of very fine needles. It is readily soluble in alcohol and ether, very slightly soluble in ligroin. It crystallizes fairly well from a mixture of equal quantities of ether and ligroin on slow evaporation of the solution. It is best purified by means of the sodium salt which is easily manipulated. If the salt is crystallized twice from alcohol, the acid precipitated from water solution by

¹⁰ Otto: Ann. Chem. (Liebig) **145**, 18.

dilute sulphuric acid and crystallized once from hot water it is obtained in a pure condition. It melts at 197°-198° without decomposition.

The sodium salt was prepared by dissolving the acid in hot sodium carbonate solution, from which the salt separated on cooling. It was dried on a porcelain plate and crystallized from boiling alcohol. The analyses show that it contains two molecules of water of crystallization, one of which can be driven off at 130°. On losing the second the salt decomposes.

- I. 0.1301 gr. salt gave 0.0254 gr. Na_2SO_4 .
- II. 0.0877 gr. salt gave 0.0172 gr. Na_2SO_4 .
- III. 0.2174 gr. salt lost 0.0117 gr. H_2O at 130°.
- IV. 0.2057 gr. salt dried at 130° gave 0.0437 gr. Na_2SO_4 .

	Calculated for $\text{C}_{10}\text{H}_{12}\text{O}_4\text{SNa} \cdot 2\text{H}_2\text{O}$.		Found.	
	I.		II.	III.
Na	6.35	6.32	6.35	
H_2O (1 mol.)	5.00			5.30

	Calculated for $\text{C}_{10}\text{H}_{10}\text{O}_4\text{SNa} \cdot \text{H}_2\text{O}$.		Found.
			IV.
Na	6.68		6.88

The salt crystallizes from alcohol in fine, shining, white needles. Its slight solubility in sodium carbonate solution and its solubility in alcohol make it easy to manipulate. It has an exceedingly bitter taste.

The calcium salt was made by boiling the acid for several hours with calcium carbonate suspended in water, and recrystallizing the product from water from which it separates in colorless plates, having a beautiful pearly lustre.

- I. 0.1683 grams salt gave 0.0330 gr. CaSO_4 .
- II. 0.1198 grams salt gave 0.0239 gr. CaSO_4 .

	Calculated for $(\text{C}_{10}\text{H}_{10}\text{O}_4\text{S})_2\text{Ca}$.		Found.	
	I.		II.	
Ca	6.18	5.73	5.85	

The barium salt was prepared in the same way. It crystallized from water in shining plates with four molecules of water of crystallization.

The barium salt was made by neutralizing the acid with barium carbonate. It crystallized in white needles moderately soluble in water, insoluble in alcohol.

0.0993 gr. salt gave 0.0310 gr. BaSO_4 .

	Calculated for $(\text{C}_{15}\text{H}_{13}\text{SO}_2)_2\text{Ba}$.	Found.
Ba	18.60	18.40

The ethyl ester was made by passing hydrochloric acid into a solution of the acid in absolute ethyl alcohol. It was purified by recrystallization from ethyl alcohol.

I. 0.1486 gr. subs. gave 0.3490 gr. CO_2 and 0.0764 gr. H_2O .

II. 0.1314 gr. subs. gave 0.3078 gr. CO_2 and 0.0670 gr. H_2O .

	Calculated for $\text{C}_{17}\text{H}_{15}\text{SO}_4$.	I.	Found. II.
C	64.15	64.05	63.89
H	5.63	5.54	5.66

The ester crystallized from alcohol in small white needles, melting at 139° . It is soluble in alcohol, insoluble in cold water, very slightly soluble in hot water. It is not changed by continued boiling with water. When boiled with dilute hydrochloric acid it is saponified to the corresponding acid. When boiled with dilute caustic potash it is decomposed, yielding cinnamic and para-toluene sulphinic acids.

3. Addition of para-toluene sulphinic acid to fumaric and maleic acids.

β-tolylsulphonepropionic acid, $\text{C}_6\text{H}_7\text{SO}_2\text{CH}_2\text{CH}_2\text{COOH}$.

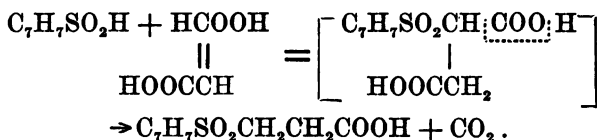
An aqueous solution of para-toluene sulphinic acid and fumaric acid, in molecular proportions, was boiled several days. A small amount of a fine, white crystalline substance separated after a few hours. This was filtered off and found to be toluene disulphoxide, due to decomposition of part of the sulphinic acid. The boiling was continued and, after forty hours, a considerable quantity of a yellowish oil had separated. After boiling for sixty hours the oil had solidified to a hard yellowish mass and the solution was filled with a quantity of shining needle-shaped crystals, some more than an inch in length. This substance was found to be an acid,

melting from 100° to 112°. It was dissolved in sodium carbonate, the solution filtered and extracted with ether to rid it of disulphoxide and the acid precipitated with dilute sulphuric acid. It was crystallized from hot water and analyzed.

0.1819 gr. subs. gave 0.3536 gr. CO₂ and 0.0990 gr. H₂O.

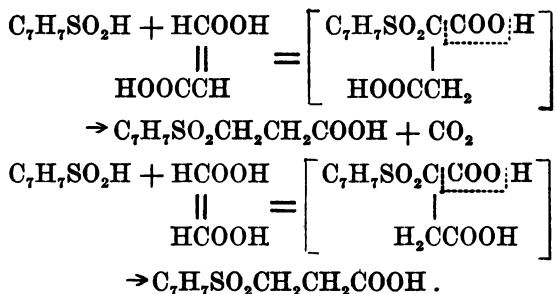
	Calculated for C ₁₁ H ₁₂ SO ₄ .	Calculated for C ₁₀ H ₁₂ SO ₄ .	Found.
C	48.5	52.58	53.01
H	4.41	5.31	6.03

Other analyses gave no better results as the acid was exceedingly difficult to purify. Analyses indicated that the substance was not the addition-product looked for, but was a mono-basic acid formed by the addition of the sulphinic acid to the fumaric acid, and the splitting off of carbon dioxide from the product according to the following equation:



The acid was precipitated from an aqueous solution of the sodium salt by dilute sulphuric acid. If the sulphuric acid were added slowly with constant stirring the substance separated in fine creamy-white needles. If the sulphuric acid were added more rapidly the acid came down as an oil which solidified on standing. It crystallizes from large quantities of water in long, needle-shaped crystals which are exceedingly brittle. They melt at 107°-114°. The substance is very slightly soluble in cold water, soluble in a considerable quantity of hot water in which it first melts down to a yellowish oil.

When maleic and para-toluene sulphinic acids were boiled in water for several hours the same acid was formed as in the reaction of fumaric with sulphinic acid. It separated from water solution in long, shining, brittle needles, melting from about 107° to 115°. The crystals were slightly soluble in cold water and melted down to an oil in hot water. It is to be expected that the same acid would be formed from maleic and fumaric acids, as is shown in the following equations:



In order to identify this acid it was made from β -iodo-propionic acid and sodium toluene sulphonate, $\text{CH}_2\text{ICH}_2\text{COOH} + \text{NaSO}_2\text{-C}_7\text{H}_7 = \text{C}_7\text{H}_7\text{SO}_2\text{CH}_2\text{CH}_2\text{COOH} + \text{NaI}$.

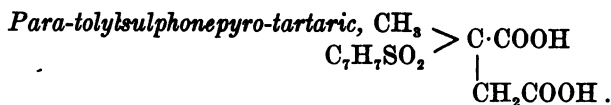
Fifty grams of β -iodo-propionic acid were exactly neutralized with sodium carbonate, the calculated amount of sodium sulphonate added and the solution evaporated to dryness on the water-bath. The dark reddish-brown residue was dissolved in a considerable quantity of dilute hydrochloric acid, and the solution decolorized with animal charcoal. On evaporating the solution slowly the acid separated in fine needles melting at $105^\circ\text{--}114^\circ$. After recrystallization from water it melted at $110^\circ\text{--}113^\circ$.

I. 0.2237 gr. subs. gave 0.4280 gr. CO_2 and 0.1076 gr. H_2O .

II. 0.1167 gr. subs. gave 0.2248 gr. CO_2 and 0.0589 gr. H_2O .

	Calculated for $\text{C}_{10}\text{H}_{12}\text{SO}_4$.	I.	Found.	II.
C	52.58	52.18		52.53
H	5.31	5.34		5.51

This acid is in all respects identical with that obtained by addition of sulphinic to fumaric and maleic acids. It crystallizes from large quantities of hot water in long, shining, creamy-white needles, which are very stiff and brittle. It is very slightly soluble in cold water and melts down to a yellowish oil in hot water. If crystallized repeatedly from hot water the acid partially decomposed, the melting point being considerably lowered. To purify it, it is best to dissolve it in sodium carbonate, extract the solution with ether to free it from disulphoxide, precipitate it with dilute sulphuric acid and crystallize once from a considerable quantity of hot water.

4. Addition of *para*-toluene sulphinic acid to citraconic acid.

Ten grams of citraconic acid and 13.5 grams of the sulphinic acid were heated in a sealed tube two days at 110°. The liquid, which contained a small quantity of fine white crystals and a little yellowish solid, was then exactly neutralized with sodium carbonate. The solid did not dissolve and a melting point determination showed it to be toluene disulphoxide. The alkaline solution was filtered, extracted twice with ether and evaporated to dryness on the water-bath. The residue was then dissolved in as small a quantity as possible of 50 per cent alcohol and the same volume of absolute alcohol was added. The sodium salt precipitated at once. It was recrystallized by the same method. It separated, with two molecules of water of crystallization in fine, pure white needles.

I. 0.2377 gram salt gave 0.0936 gr. Na_2SO_4 .

II. 0.2140 gram salt gave 0.0833 gr. Na_2SO_4 .

III. 0.3277 gram salt lost 0.0326 gr. H_2O at 150°.

	Calculated for $\text{C}_{11}\text{H}_{13}\text{SO}_6\text{Na}_2 \cdot 2\text{H}_2\text{O}$.		Found.	
	I.		II.	III.
Na	12.60	12.65	12.65	
$2\text{H}_2\text{O}$	9.84			9.96

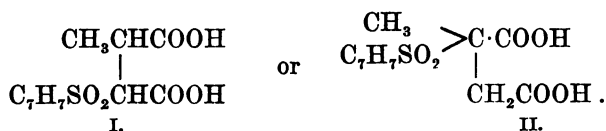
On acidifying the aqueous solution of this salt with dilute sulphuric acid the acid was obtained as an oil. This was taken up with ether and the solution evaporated to comparatively small volume. Ligroin was then slowly added until the solution was slightly cloudy. On addition of a drop of ether the solution again became clear and the acid separated slowly in small, shining white prisms. It is necessary to have the proportions of ether and ligroin exactly right, otherwise the acid does not crystallize out but separates as an oil which solidifies after long standing.

0.4118 gr. subs. gave 0.2226 gr. CO_2 and 0.0979 gr. H_2O .

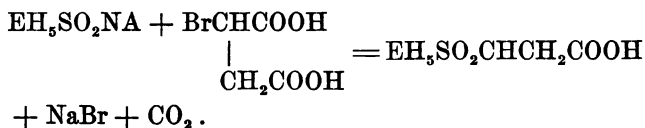
	Calculated for $\text{C}_{12}\text{H}_{14}\text{SO}_6$.	Found.
C	50.35	50.45
H	4.89	4.88

The acid is extremely soluble in alcohol, ether, glacial acetic acid and acetone. It is insoluble in ligroin and chloroform. If precipitated from sodium carbonate solution it separates as an oil which does not solidify. It melts at 169° - 171° and begins to lose carbon dioxide as soon as melted.

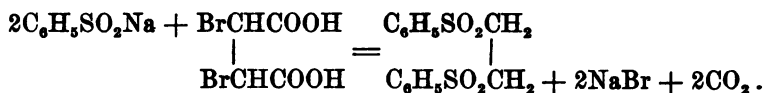
The fact that this acid loses carbon dioxide so readily seemed to furnish a possible method for determining its structure by driving off carbon dioxide and identifying the residue. Five grams of acid were heated on an oil bath at 180° for two hours. There was a rapid evolution of carbon dioxide but, at the same time, the acid decomposed into sulphur dioxide and a small quantity of a clear liquid which distilled over at 190° and solidified on standing. This attempt, therefore, to prove the structure was without result. However, there can be no doubt as to the way in which the sulphinic acid adds to the citraconic acid when one takes into consideration the following facts. There are two possible formulas for the addition-product of the para-toluene sulphinic acid to the citraconic:



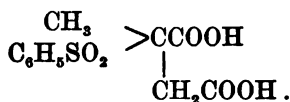
It has been shown that when toluene sulphinic acid combines with maleic and fumaric acids, carbon dioxide is lost from the intermediate addition-product and a mono-basic acid is formed. It is known that monobromsuccinnic acid when treated with sodium benzene sulphinate loses carbon dioxide and forms β -phenyl sulphonepropionic acid:



In the same way sodium benzene sulphinate, acting on symmetrical dibromsuccinnic acid, splits off two molecules of carbon dioxide to form ethylene di-phenyl sulphone:

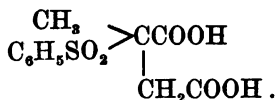


These reactions indicate that the sulphone group has an influence on the molecule analogous to that of a carbonyl group or a halogen atom in that it causes the loss of carbous dioxide from the neighboring carboxyl group. Examples of this influence of halogen atoms are found in the substituted malonic and succinnic acids. Malonic acid loses carbon dioxide at 180° , mono-brom-malonic at 150° , di-brom at 100° . Succinnic acid does not lose carbon dioxide on heating but forms an anhydride. Unsymmetrical di-brom-succinnic acid, on the other hand, loses carbon dioxide and not water. If the product of the addition of toluene sulphinic to citraconic acid has the structure represented in formula I, it is to be expected that the presence of the sulphone group would lead to a loss of carbon dioxide. If it has formula II, however, the influence of the sulphone group would not be felt, as it would be counteracted by the methyl group. Since carbon dioxide is not given off from this acid, which differs from the addition-product of sulphinic to maleic acid only in the presence of the methyl group, it is undoubtedly the influence of this methyl group which has counteracted the influence of the sulphone group and the structure of the acid is, therefore:



5. Addition of benzene sulphinic acid to mesaconic acid:

Phenylsulphonepyro-tartaric acid,



Ten grams of mesaconic acid were boiled in water with the calculated amount of benzene sulphinic acid for two days. Most of the water was then distilled off. The acid separated slowly from the solution. It is insoluble in petroleum ether, readily

soluble in water and ether. It was very hard to purify and no analyses were made. The sodium salt was prepared and purified as in the case of the citraconic acid. It separated in beautiful colorless plates:

- I. 0.1989 gr. salt gave 0.0892 gr. Na_2SO_4 .
 II. 0.1342 gr. salt gave 0.0598 gr. Na_2SO_4 .

Calculated for $\text{C}_{11}\text{H}_{10}\text{SO}_3\text{Na}_2$		Found.	
		I.	II.
Na	14.60	14.58	14.44

IV. ADDITION OF PARA-TOLUENE SULPHINIC ACID TO KETONES.

Sulphinic acids do not combine with saturated ketones. Acetone and acetophenone were heated with para-toluene sulphinic acid in aqueous, alcoholic and ethereal solutions but in each case the unchanged sulphinic acid was recovered.

1. Addition of para-toluene sulphinic acid to dibenzalacetone.

Para-toluene sulphinic acid combines with dibenzalacetone with the greatest ease. If a solution of the acid in alcohol be added to a solution of the unsaturated ketone in the same solvent, and the mixture allowed to stand in the cold, the yellow color of the solution disappears and a product separates, in fine white needles. This can be purified by repeated crystallization from alcohol or benzene. An analysis gave the following results:

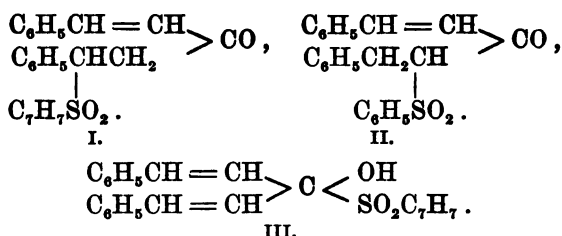
0.1856 gr. subs. gave 0.5020 gr. CO_2 and 0.0973 gr. H_2O .

Calculated for $\text{C}_{17}\text{H}_{14}\text{O} \cdot \text{HSO}_3\text{C}_7\text{H}_7$		Found.
C	73.82	73.76
H	5.64	5.82

These results show that the substance contains one molecule of the sulphinic acid in combination with one of the ketone. To determine whether this is the only way in which the substances combine, two equivalents of the sulphinic acid were sealed up in a tube with one equivalent of the ketone. The tube was kept at a temperature of 110° for two days. The white solid which separated out proved to be the substance which had been obtained in the cold. The excess of sulphinic acid had been transformed

into para-toluene disulphoxide, which crystallized from the solution on evaporation. A similar result was obtained when the addition-product obtained in these experiments was heated with a second equivalent of sulphinic acid. It is evident, therefore, that but one molecule of the sulphinic acid combines with one of dibenzalacetone.

For an addition-product having this composition there are three possible formulas:



The simplest way of distinguishing between these formulas is by oxidation.

One and six-tenths grams of potassium permanganate were added to a solution of two grams of the substance in glacial acetic acid and the mixture heated on the water-bath for an hour. The dark brown solution, which had a strong odor of benzaldehyde, was decolorized with sulphur dioxide. A pasty, white mass separated. Water was added till this solid dissolved and steam was then passed through the boiling, aqueous solution to free it from benzaldehyde and benzoic acid formed by oxidation. On cooling, a white, flocculent, crystalline substance separated from the aqueous solution. This was filtered off and dissolved in hot sodium carbonate. A sodium salt separated from the solution on cooling. This salt crystallized from alcohol in long, shining white needles, having an exceedingly bitter taste. It was dissolved in water and dilute sulphuric acid was added. An acid separated in very fine white needles, which melted, after recrystallization from boiling water, at $196^\circ\text{--}197^\circ$. The acid was β -para-sulphone hydro-cinnamic acid, $\text{C}_6\text{H}_5\text{CHCH}_2\text{COOH}$, previously obtained by addition of para-



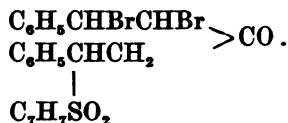
toluene sulphinic acid to cinnamic acid. When crystals of this

latter substance were intimately mixed with those of the oxidation product they melted at 196°-197°, the temperature at which each substance melts when heated by itself.

The addition of the sulphinic acid to the benzalacetone, therefore, takes place at one of the double linkages, the sulphone group going to the β -carbon atom, to form a sulphone ketone whose structure is represented by formula I.

The sulphone ketone crystallizes from alcohol in fine white needles, melting at 189°. It is soluble in alcohol, ether and glacial acetic acid, insoluble in water and ligroin. Hot, concentrated hydrochloric acid decomposes it into benzalacetone and toluene disulphoxide. Boiling aqueous sodium hydroxide has very little effect on the substance, but alcoholic potash splits off the sulphinic acid.

It is remarkable that the sulphone ketone does not combine with a second molecule of sulphinic acid since it combines with two atoms of bromine, to form the compound:

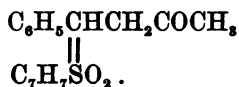


Two grams of the sulphone ketone were dissolved in chloroform and eight-tenths of a gram of bromine added. After standing three days, the solution, which was, at first, a deep red, had become pale yellow. The chloroform was distilled off and the white solid which remained was crystallized from alcohol. The following analysis shows that the sulphone ketone has combined with two atoms of bromine:

0.1557 gr. subs. gave 0.1058 gr. AgBr.

	Calculated for $\text{C}_{12}\text{H}_{12}\text{SBr}_2\text{O}_2$.	Found.
Br	29.09	28.85

The bromine addition-product crystallized from alcohol in fine, white needles, very closely resembling the original substance. It is soluble in alcohol, very soluble in chloroform, insoluble in ether, acetone, glacial acetic acid and water. It melts with decomposition at 204°, giving off a gas as soon as melted.

2. *Addition of para-toluene sulphinic acid to benzalacetone:*

Benzalacetone like, di-benzalacetone, combines with para-toluene sulphinic acid in the cold. To prepare the addition-product in quantity, alcoholic solutions of the sulphinic acid and benzalacetone in molecular proportions were brought together and heated on the water-bath. A copious, white precipitate separated after a few minutes. This product was crystallized from alcohol several times and obtained in fine, white needles. An analysis gave the following results:

0.2322 gr. subs. gave 0.5737 gr. CO_2 and 0.1251 gr. H_2O .

	Calculated for $\text{C}_{17}\text{H}_{18}\text{SO}_2$.	Found.
C	67.54	67.38
H	5.96	5.98

The compound is readily soluble in acetone, moderately soluble in boiling alcohol and boiling benzene, sparingly soluble in cold alcohol and ether, insoluble in water. It separates from alcohol in aggregates of fine, white needles, which change into a much more compact form after the solution has cooled.

Reaction of the sulphone ketone toward phenyl hydrazine.

Two grams of the sulphone ketone were dissolved in alcohol, seven-tenths of a gram of phenyl hydrazine added, and the solution boiled for two hours. On evaporation of the alcoholic solution, crystals separated. These were found to be of two kinds, some very soluble in ether in the cold, and other, smaller crystals only soluble in boiling ether. The two substances were, therefore, separated by extracting several times with ether in the cold. To the ether extract, which was colored a reddish-yellow, the same volume of alcohol was added and the solution evaporated until the ether had been driven off. Water was then added till the solution became a little cloudy. Fine yellow crystals began to separate at once, and, after cooling, the solution was filled with long, brittle needles of a bright, lemon-yellow color. The substance was re-crystallized from dilute alcohol. It melted, without change, at

159°. This substance is the phenyl hydrazone of benzalacetone.¹² It was compared with specimens made directly from benzalacetone and phenyl hydrazine and found to be identical.

The crystals which separated from the original alcoholic solution and were not soluble in ether in the cold, were dissolved in a considerable quantity of boiling ether. The ethereal solution was of a pale, straw color with a bluish-green fluorescence. It was evaporated to small volume and ligroin added. A quantity of fine white needles separated. This substance was redissolved in ether and reprecipitated by ligroin and then crystallized from ether, from which it separated in small, white needles, melting at 165°.

0.1126 gr. subs. gave 0.2450 gr. CO₂ and 0.0563 gr. H₂O.

	Calculated for C ₇ H ₇ SO ₂ H · H ₂ N · NHEH ₅ .	Found.
C	59.08	59.32
H	6.06	5.55

The substance is, therefore, the phenyl hydrazine salt of para-toluene sulphinic acid. It is soluble in alcohol, moderately soluble in ether, insoluble in water and ligroin. It begins to decompose at 160° and melts at 165°. A gas is given off as the substance melts. This salt was also prepared by heating an alcoholic solution of the sulphinic acid with phenyl hydrazine. It separated from the alcoholic solution, on slow evaporation, in long, brittle, creamy-white needles. It oxidizes easily when the ethereal solution is left standing in the air.

The mother-liquor, from which the phenyl hydrazone of benzalacetone and the phenyl hydrazine salt of para-toluene sulphinic acid had separated, deposited a third substance, on slow evaporation. This substance crystallized in long, red needles. It was recrystallized several times from alcohol, and when pure was obtained as long, branching, straw-colored crystals, melting, without change, at 114°.

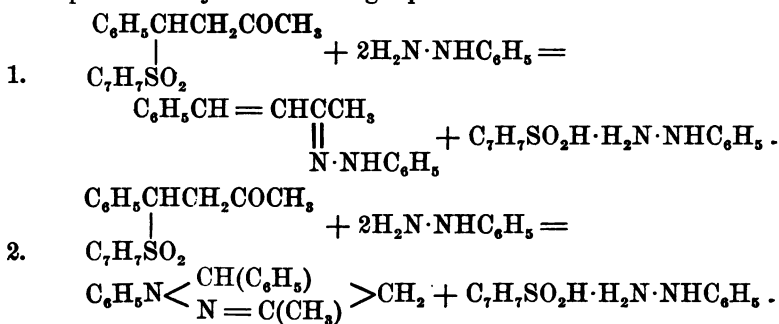
0.2031 gr. subs. gave 0.6047 gr. CO₂ and 0.1251 gr. H₂O.

	Calculated for C ₁₀ H ₁₀ N ₂ .	Found.
C	81.35	81.19
H	6.78	6.84

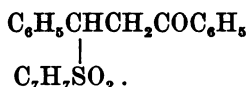
¹² Knorr, Ber. d. chem. Ges., 20, 1098.

The compound gives a deep blue color with nitrous acid and the characteristic reddish-purple color of the pyrazol derivatives when treated with ferric chloride in acid solution. It is 1, 5 di-phenyl, 3 methyl pyrazoline.¹³

The action of phenyl hydrazine upon the sulphone ketone may be represented by the following equations:



3. *Addition of para-toluene sulphinic acid to benzalacetophenone:*



One gram of the sulphinic acid was added to a hot alcoholic solution of one gram of benzalacetophenone. A white crystalline solid separated at once. It was recrystallized from alcohol and analyzed:

0.2574 gr. subs. gave 0.6826 gr. CO₂ and 0.1186 gr. H₂O.

	Calculated for C ₂₂ H ₂₀ SO ₂ .	Found.
C	72.52	72.32
H	5.49	5.12

The substance crystallizes from alcohol in small white needles, which melt at 169°-170°.

Colorless, crystalline products, similar to those described, were obtained when para-toluene sulphinic acid was added to an alcoholic solution of para-nitro-benzaldehyde, and to ethereal solutions of piperonalacetone and di-piperonalacetone. These substances are, undoubtedly, addition-products analogous to those described.

¹³Knorr: Ber. d. chem. Ges., 20, 1098.

CONCLUSION.

In the experiments described it has been shown that sulphinic acids combine with aldehydes and with unsaturated acids and ketones.

By the addition of sulphinic acids to aldehydes, oxysulphones are formed. The method has been found to be of general application and it is of value for the preparation of this class of substances, as attempts to make oxysulphones by other methods have been unsuccessful.¹⁴

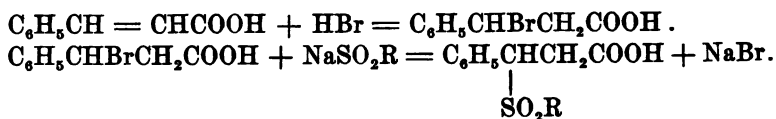
The oxysulphones are crystalline compounds which are very unstable. This instability is due to the fact that the reaction between aldehydes and sulphinic acids is a reversible one according to the equation: $\text{RCHO} + \text{HSO}_2\text{R}' \rightleftharpoons \text{RCH} < \begin{smallmatrix} \text{OH} \\ \text{SO}_2\text{R}' \end{smallmatrix}$, and only under special conditions can the oxysulphones be isolated. In this respect these substances differ widely from the corresponding oxysulphonic acid salts, formed by the addition of acid sulphites to aldehydes. The latter are comparatively stable, crystalline compounds, easily formed and isolated.

The addition of toluene sulphinic acid to saturated aldehydes takes place with the greatest ease. The substances combine at the ordinary temperatures in the absence of a solvent or in alcoholic or ethereal solution. This is analogous to the action of potassium acid sulphite on unsaturated aldehydes. The acid sulphite addition-products of acrolein, crotonic aldehyde and cinnamic aldehyde are formed with great ease.

It has been shown that sulphinic acids combine with many substances containing doubly-linked carbon atoms, experiments having been described with unsaturated acids and ketones. No reaction took place when unsaturated hydrocarbons were treated with sulphinic acids. Experiments were tried with para-toluene sulphinic acid and amylene and styrene in aqueous, alcoholic and ethereal solutions, but no addition-products were obtained, nor was there any evidence of a reaction.

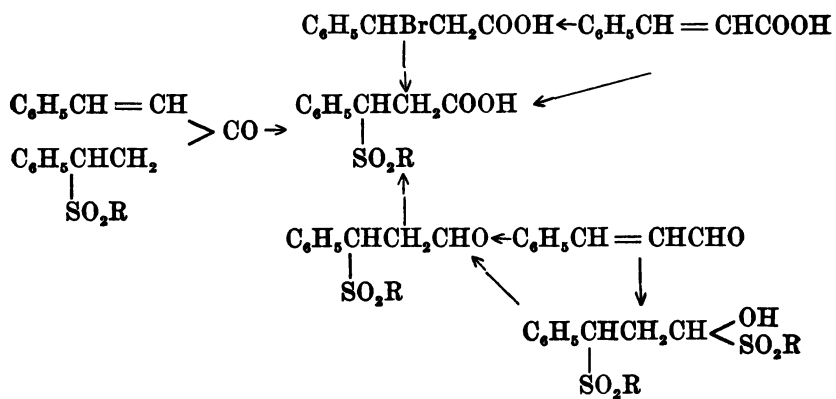
¹⁴Laves: Ber. d. chem. Ges. 25, 347.

The ease with which these reactions take place depends upon the nature of the substances. The addition of sulphinic acids to unsaturated ketones takes place with the greatest ease. The substances combine, in many cases, in the cold, in all, with slight heating, and the products are sparingly soluble in the alcoholic or ethereal solution used as a medium for the reaction, so that they are easily isolated. The sulphone ketones, thus formed, are perfectly stable, crystalline compounds. This reaction with ketones is of value, as no direct method for the preparation of β -sulphone ketones has, up to this time, been known. The unsaturated ketones do not combine with hydrochloric acid nor hydrobromic acid, so that it is impossible to introduce a sulphone group by the action of a sodium sulphinate on a halogen acid addition-product of the ketone, a method which is possible in the case of unsaturated acids:



The addition of sulphinic acids to unsaturated acids takes place most readily when the substances are boiled in water for several hours or are heated, in water, in a sealed tube. The reactions with aldehydes are best carried on in ethereal solution.

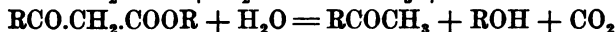
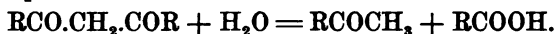
In all cases in which the structure of the addition-products was investigated, it was found that whenever sulphinic acids add to α , β -unsaturated aldehydes, acids or ketones, the sulphone group goes to the β position with reference to the carbonyl group. When the sulphinic acids combine with di-basic acids in which there is double linkage between two α carbon atoms, carbon dioxide is given off and a mono-basic acid is formed in which the sulphone group is attached to the β carbon atom. The only exception to this is found in those cases in which the negative influence of the sulphone group is counteracted by some positive influence, as that of the methyl group in citraconic and mesaconic acids. The way in which the structure of the compounds was established is shown by the following diagram:



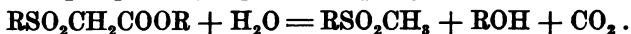
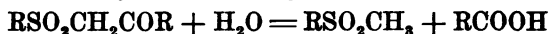
A NEW CLASS OF DISULPHONES

By a comparison of the compounds of carbon and sulphur many striking analogies are brought to light. These are seen most clearly when carbon compounds are compared with those organic sulphur compounds which contain quadrivalent or hexavalent sulphur, as for example, sulphonic acids and sulphones.

The sulphonic acids form chlorides, substitution products, anhydrides and salts which resemble closely the corresponding derivatives of carbonic acids in composition, structure and essential properties. The analogy between ketones and sulphones is more striking even than that of sulphonic and carbonic acids. The simple sulphones, RSO_2R , like the corresponding ketones, RCOR , are indifferent substances, which boil without decomposition, and which are not readily attacked by reagents. Polyketones are much more reactive than monoketones. All 1, 3 diketones and 1, 3 ketonic acid esters for example, are readily hydrolyzed according to the equations:



All 1, 3 sulphone ketones and 1, 3 sulphone carbonic acid esters behave in exactly the same way:



In these reactions the RSO_2 -group is exactly equivalent to the RCO -group.

The 1, 3 disulphones are more stable than the corresponding diketones and sulphone ketones; but like the latter they form metallic derivatives in which the metal is replaceable by hydrocarbon residues.

The researches of Otto,¹ Baumann,² Autenried,³ and Posner⁴

¹ Ber. d. chem. Ges., 18, 154; 21, 89; 18, 2493.

² Ber. d. chem. Ges., 19, 2806.

³ Ber. d. chem. Ges., 24, 1891.

⁴ Ber. d. chem. Ges., 32, 1239.

have led to the discovery of the sulphur analogues of nearly all classes of polyketones. The only important class that is missing is that of 1,2 disulphones;



A disulphone of this type would be especially interesting because it would differ from all known organic sulphur compounds in having two hexavalent sulphur atoms in direct union. It is known that organic compounds containing two sulphur atoms in direct union, are capable of existence. The aliphatic and aromatic disulphides, for example, are stable substances containing two bivalent sulphur atoms in direct union: R-S-SR. The well crystallized thio ethers, or disulphoxides, RSO_2 , undoubtedly also

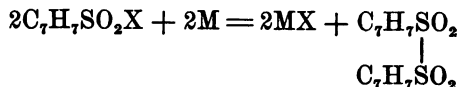


contain two sulphur atoms in direct union, and one of the sulphur atoms must be hexavalent, while the other is bivalent. There seems to be no reason, therefore, why compounds containing two hexavalent sulphur atoms should not be capable of existence.

It has been the object of this investigation to determine whether such substances are capable of existing and, if possible, to prepare and study disulphones of the type represented by the formula,



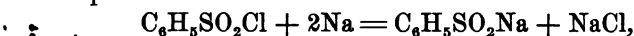
Several previous attempts have been made to secure this class of substances. Otto, whose name is so intimately associated with all classes of sulphones, attempted to prepare α , β -disulphones by the methods used for linking carbon atoms together. It was expected that, on the removal of the halogen from two molecules of a sulphone halide, the residues would unite to form a disulphone:⁵



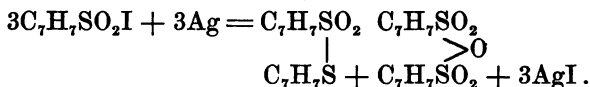
Otto found, however, that the reactions which take place when

⁵ Ber. d. chem. Ges., **24**, 478.

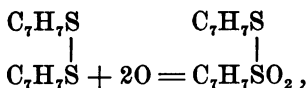
sulphone halides are treated with metals, are much more complicated than that represented by this equation, and that they do not lead to the formation of the desired sulphone. Thus, benzenesulphone chloride, when treated with sodium, gave sodium benzenesulphinate:



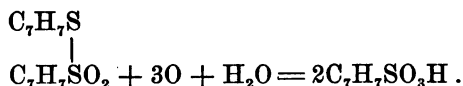
while toluenesulphone iodide, when heated with finely divided silver, reacted according to the equation:



It would also seem possible to obtain such sulphones by the oxidation of the disulphides RS.SR , but by this method only one of the sulphur atoms is oxidized to the hexavalent condition, the reaction resulting in the formation of a thio-ether:



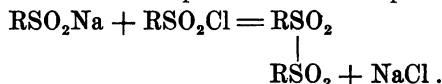
On further oxidation the union between the sulphur atoms is broken:



The failure of these attempts to prepare the disulphone by the methods applicable in the case of carbon compounds led Otto⁶ to conclude that these substances are incapable of existence. A more recent investigator⁷ has arrived at the same conclusion. All that these results show, however, is that these disulphones can not be made by the methods regularly used for establishing carbon linkages.

Of all possible methods of preparation the following seemed most likely to lead to the desired result.

1. Reaction between a sulphinate and a sulphone halide, thus:



⁶ Ber. d. chem. Ges., **24**, 484.

⁷ Turner, Amer. Chem. Jour., **21**, 125.

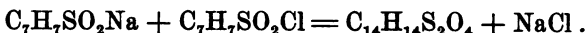
disulphone. A similar mixture was heated in a sealed tube to 100° for eight hours, and to 120°-130° for eight hours more. Decomposition took place, but no disulphone was formed.

3. *In alcoholic solution.*

To a concentrated solution of sodium para-tolylsulphinate in absolute alcohol, an equivalent amount of para-tolylsulphone chloride was added, and the mixture kept at the boiling point of alcohol for several hours. There was no appearance of a disulphone at any time.

4. *In aqueous solution.*

Sodium para-tolylsulphinate was dissolved in the least possible quantity of water. A proportional amount of powdered para-tolylsulphone chloride was added to this solution. The mixture was heated on the water-bath to 70°. At this temperature the chloride melted. The contents of the flask were well shaken, and the chloride almost immediately disappeared. The disappearance of the chloride was followed by the separation of a solid. This solid product was placed on a filter, washed repeatedly with boiling water and finally with ether, dried, and weighed. The yield of crude product was 20 per cent of that calculated according to the equation:



The crude product was not, however, as pure as it was desirable to have it.

5. *In ether and water.*

Para-tolylsulphone chloride was dissolved in a flask in the smallest possible quantity of ether and to this was added a saturated water solution of the calculated amount of sodium para-tolylsulphinate. The flask, which was connected with a return condenser, was heated on a water-bath, and shaken occasionally. In a short time a solid appeared as a scum between the two layers of liquid. The heating was continued until no more solid seemed to form, or until the sulphone chloride had disappeared. The duration of the heating varied in different experiments from six to thirty hours. Although continued heating was apparently necessary, it could not be determined that time entered as a

definite factor into the reaction. The hot solution was filtered, and after the evaporation of the ether, was found to contain sulphinic acid. This was neutralized with sodium carbonate, more of the sulphone chloride in ether solution was added, and the mixture again heated. A small additional quantity of the solid product usually separated out.

The filtrate was acidified with sulphuric acid and the sulphinic acid precipitated. This was filtered off, and the filtrate extracted with ether for the removal of any sulphinic acid that had escaped precipitation. This was identified by its melting point. The extracted solution was neutralized with sodium hydroxide and evaporated to dryness. The residue was then extracted with absolute alcohol. The sodium sulphonate thus obtained was acidified and the melting point of the acid determined. The filtrate from the disulphone contained therefore, para-tolylsulphonic acid, para-tolylsulphinic acid and sodium chloride.

The solid, after being washed repeatedly with boiling water to remove any adherent sodium para-tolylsulphinate, dried on the water-bath and washed with boiling ether to extract any unchanged para-tolylsulphone chloride, is white, crystalline, and comparatively pure.

While this method gave an unusually pure product, the yield was small, as the amount of crude substance was only 12-20 per cent of that calculated. With the hope of improving the yield, sulphinates of other metals were prepared and substituted for the sodium sulphinate.

6. *Zinc para-tolylsulphinate and para-tolylsulphone chloride.*

The zinc salt was prepared by reducing the chloride with zinc dust and recrystallizing the product from large quantities of water. A calculated amount of zinc para-tolylsulphinate was added to an ether solution of a weighed quantity of para-tolylsulphone chloride. To this was added a mixture of alcohol and water. The final mixture was heated on the water-bath for an hour, and then allowed to stand over night at the temperature of the laboratory. The zinc sulphinate dissolved, and a very small quantity of disulphone formed. The yield was very poor—the crude product was mixed with much unchanged zinc sulphinate.

7. *Ammonium para-tolylsulphinate and para-tolylsulphone chloride.*

The ammonium salt of para-tolylsulphinic acid was prepared by dissolving the acid in dilute ammonia. It crystallized from this solution in beautiful, colorless, transparent, monoclinic crystals with a melting point of 164° - 167° . When recrystallized from water, the melting point remained 164° - 167° , bubbles of gas being evolved above 164° .

A concentrated water solution of ammonium para-tolylsulphinate was added to an ether solution of the sulphone chloride. After the mixture was heated for several hours a small quantity of the di-sulphone appeared. This did not increase in amount after the first day, although the heating was continued for six days. After the product was washed with water and ether, it was comparatively pure but small in quantity, the yield being only about 4.5 per cent.

8. *Silver para-tolylsulphinate and para-tolylsulphone chloride.*

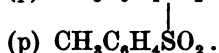
The silver sulphinate was prepared by adding a slight excess of silver nitrate to a solution of the sodium salt. It separated as a white, amorphous precipitate, which was filtered and dried with difficulty. Silver para-tolylsulphinate is a white powder, very sensitive to light. It is insoluble in water, methyl alcohol, ethyl alcohol, ether, chloroform and benzene; hence it was not recrystallized. The preparation used in the following experiment was almost white and non-crystalline.

A mixture of equivalent quantities of para-tolylsulphone chloride in ether solution and silver para-tolylsulphinate in a volume of water equal to twice that of the ether, was heated in a flask with a return condenser. The temperature was kept at that of boiling ether for several days. There was apparently no action except the decomposition of the sulphone chloride by the water, and of the silver salt by the light. No reaction between the sulphone chloride and silver salt, resulting in the formation of the di-sulphone, took place. The failure to react may be due to the insolubility of the silver sulphinate.

The amount of di-sulphone resulting from zinc sulphinate, ammonium sulphinate, or silver sulphinate was, in every instance, less than that obtained from sodium sulphinate. The sodium

sulphinate was, therefore, considered the best salt to use in the preparation of the di-sulphones.

I. DI-PARATOLYLDISULPHONE.



As a result of the experiments already described, and of others, the method adopted for the preparation of di-paratolyldisulphone was as follows:

Fifty-five grams sodium para-tolylsulphinate was dissolved in the least possible quantity of water. This was added to 58.3 grams para-tolylsulphone chloride dissolved in the least possible quantity of ether. The flask containing the mixture was fitted with a return condenser and heated on the water-bath. The temperature was kept at the boiling point of ether until there was no longer any unchanged sulphone chloride. The hot solution was filtered, after the evaporation of the ether. The white, crystalline solid was washed repeatedly with boiling water, dried on the water-bath, and washed with ether, with which it was allowed to stand in contact for about twenty-four hours with occasional agitation. It was then put upon a filter, washed with ether and dried. The crude di-sulphone was dissolved in boiling benzene, from which most of it crystallized on cooling. The remainder was obtained by the evaporation of the benzene, and was recrystallized from benzene. Since the substance still contained a small quantity of the sulphone chloride, the two portions were again washed with ether, redissolved in boiling benzene and allowed to crystallize as before. The weight of this purified product was 15 grams. The theoretical yield from 55 grams sodium para-tolylsulphinate is 84 grams. The yield of purified di-sulphone was, therefore, 18 per cent.

Di-paratolyldisulphone is a white, crystalline solid insoluble in water, methyl alcohol or ethyl alcohol. It is very difficultly soluble in chloroform, more soluble in boiling benzene or glacial acetic acid. Of the last two solvents, benzene is probably the better. The substance separates on cooling its benzene solution, in small lustrous plates that adhere to the sides and bottom of the vessel. By the spontaneous evaporation of the cold solution, or the slow

cooling of the boiling solution, the crystals may attain a diameter of 5-6 millimeters. They are thick monoclinic tables, very brittle and harder than sodium chloride. The substance melts with decomposition at 220° .

An analysis of the substance gave the following results:

I. 0.1551 gram substance gave 0.3073 gram CO_2 and 0.0597 gram H_2O .

II. 0.1609 gram substance gave 0.3196 gram CO_2 and 0.0621 gram H_2O .

III. 0.1273 gram substance gave 0.2041 gram BaSO_4 .

IV. 0.1960 gram substance gave 0.2919 gram BaSO_4 .

V. 0.1503 gram substance gave 0.2259 gram BaSO_4 .

	Calculated for ($\text{C}_7\text{H}_7\text{SO}_2$) ₂	I.	II.	Found. III.	IV.	V.
C	54.19	53.9	54.1			
H	4.51	4.26	4.3			
S	20.64			20.49	20.45	20.64

A molecular weight determination by the cryoscopic method with naphthalene as the solvent, gave the following results:

I. 1.63 grams substance per 100 grams of solvent gave a mean depression of 0.355° .

II. 2.53 grams substance per 100 grams of solvent gave a mean depression of 0.565° .

III. Constant for naphthalene, 70.

	Calculated for ($\text{C}_7\text{H}_7\text{SO}_2$) ₂	Found. I.	II.
Molecular weight	310.0	321.0	313.0

Di-paratolyldisulphone is remarkable for its inertness. It is not decomposed by mineral acids under ordinary conditions of temperature and pressure. At ordinary pressure the substance is not affected in the least degree by concentrated hydrochloric acid. Two-tenths of one gram of the powdered di-sulphone of melting point 220° , was boiled with 20 cubic centimeters concentrated hydrochloric acid for five hours without decomposition. After dilution with water the liquid was filtered off and the solid washed with water, dried and weighed. The result was 0.195 gram of solid which melted at 220° .

Decomposition is, however, effected by heating the di-sulphone with concentrated hydrochloric acid under pressure. After 0.8 gram of substance and 20 cubic centimeters of concentrated hydrochloric acid were put in a tube, the tube was sealed and heated in a bomb-furnace for about six hours to 110° - 120° , and for eight hours to 120° - 130° without any change in the appearance of the contents of the tube. After the mixture had stood for forty hours there were a few small brown patches, which gave evidence of some reaction. The heating to 125° - 130° was continued for seven hours longer, and the tube allowed to stand for two days. When opened it showed diminished pressure. Addition of water to the acid and brown oily mass caused the separation of a white solid, which, when freed from the oily substance, washed, and recrystallized from benzene, gave a melting point of 218° , with decomposition. It was unchanged di-sulphone. The oily mass consisted of a brown tar, para-tolylsulphinic acid melting at 84° , para-tolylsulphonic acid melting at 92° , and a little inorganic material. The tar, which possessed a cresol-like odor, was distilled with steam, but the quantity was too small to permit of any decisive test.

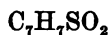
Di-paratolyldisulphone is difficultly soluble in boiling concentrated nitric acid, and crystallizes from this solution unchanged. Two-tenths of one gram of the di-sulphone was dissolved in 75-100 cubic centimeters of concentrated nitric acid. One hundred and sixty-four thousandths of a gram of substance melting with decomposition at 220° crystallized from this nitric acid solution on standing for a short time. The mother liquor, on evaporation, deposited a less pure substance, weighing 0.03 gram, and melting with decomposition at 217° . Protracted contact with fuming nitric acid led to the oxidation of the di-sulphone to carbon dioxide, water, and sulphuric acid.

When treated with fuming sulphuric acid in the cold, the di-sulphone immediately dissolved, giving a red-brown solution. This solution became milky when poured into water. From the diluted solution, sulphinic acid was extracted with ether and identified by its melting point. The acid solution, after extraction, was neutralized with sodium hydroxide, evaporated to dryness and extracted with absolute alcohol, but no sodium para-tolylsulphonate was found. While the reaction is not a simple one, sulphinic acid

constitutes the principal product. The decomposition with fuming sulphuric acid is therefore, similar to that effected by concentrated hydrochloric acid in a sealed tube.

A mixture of concentrated sulphuric and nitric acids brought about no decomposition, even when heated. The substance was merely less soluble in the mixture than in concentrated nitric acid alone.

Di-paratolyldisulphone is not attacked by alkalis in the cold, but is decomposed by boiling concentrated potash. One and one-half grams of the di-sulphone was boiled with 4 cubic centimeters of potassium hydroxide (2:3) for twenty minutes. Small quantities of water were added to supply that lost by evaporation. The di-sulphone dissolved completely. A portion of the solution was treated with zinc and acid. A strong odor of mercaptan resulted, indicating the presence of a sulphinic acid. The ether extract of the acidified solution deposited para-tolylsulphinic acid, which melted at 85°-86°. The acid solution was neutralized and evaporated to dryness. The residue was extracted with absolute alcohol. A water solution of the sodium para-tolylsulphonate which crystallized from the alcohol solution, was acidified with sulphuric acid. From this solution para-tolylsulphonic acid, melting at 91°, separated. This was dried and treated with phosphorus pentachloride. The resulting sulphone chloride, after crystallization from ether, melted at 68°-69°, the melting point of para-tolylsulphone chloride. The decomposition with alkalis must therefore be in accordance with the equation:



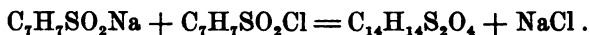
All attempts to effect a decomposition by boiling with water, or with very dilute alkalis, failed, although the boiling was continued for seven or eight hours.

An attempt was made to oxidize di-paratolyldisulphone, in acetic acid solution, with potassium permanganate solution, but without success. Into a hot solution of 2 grams di-sulphone in acetic acid, 300 cubic centimeters of a 5 per cent solution of potassium permanganate was slowly dropped as fast as the solution became colorless. After about forty hours the process was stopped and

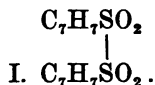
the clear solution filtered off. Nothing but a small quantity of inorganic matter was found in the acid solution. The oxides of manganese were extracted with boiling benzene, and 1.9 grams of the unchanged di-sulphone crystallized out. After recrystallization from benzene the di-sulphone melted with decomposition at 220° . A blank test was made with some of the same acetic acid and potassium permanganate solution. Decoloration took place about as rapidly as when the di-sulphone was present. The reduction of the permanganate was therefore due to the acetic acid and not to the di-sulphone.

Proof of Structure.

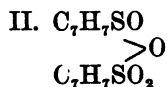
The formation of the solid substance, described as di-sulphone, undoubtedly takes place according to the equation:



That this reaction does not take place in the absence of water, and that a very small quantity of water is sufficient has been demonstrated, but it has not been possible to determine what rôle the water plays. The reaction, however, supplies a clue to the structure of the product. Two possibilities present themselves, depending on the desmotropic nature of sulphinic acids. If the sulphinate reacts according to the generally accepted formula, $C_7H_7SO_2$, then the product must be a di-sulphone with the structure represented by the formula:



If, however, the formula of the sulphinate is $C_7H_7SO_2$, then the substance might be an anhydride with the structure represented by the formula:



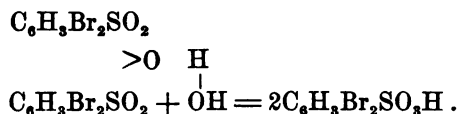
The anhydrides of sulphonic acids are, for the most part, extremely reactive substances, similar in behavior to sulphur trioxide, the

² Ber. d. chem. Ges. 18, 2493.

anhydride of sulphuric acid. They readily react with water and alcohol to form sulphonic acids and sulphonic acid esters. A mixed anhydride of a sulphinic and a sulphonic acid, like that represented by formula II, would be expected to be equally sensitive to these reagents. It has been shown, however, that the substance under consideration is exceedingly inert. It is not hydrolyzed by boiling with water, dilute alkalis or acids. It may even be crystallized unchanged from a solution in concentrated nitric acid. This behavior is in favor of the di-sulphone formula. It would seem incredible that an anhydride containing a sulphinic acid residue could resist hydrolysis and oxidation by concentrated nitric acid.

A peculiar class of anhydrides of sulphonic acids has been described by Rosenberg.* Rosenberg found that when para-dibromobenzene is treated with fuming sulphuric acid it is converted into the anhydride of para-bromobenzene sulphonic acid, an inert substance melting at a high temperature, insoluble in water, but soluble in alcohol without decomposition. Armstrong¹⁰ found that only sulphonic acids derived from halogen substitution products of benzene form anhydrides of this kind.

For purposes of comparison, para-dibromobenzene sulphonic anhydride was made by the method of Rosenberg, modified as follows: A mixture of di-bromobenzene and fuming sulphuric acid in the proportion of 2 grams of the former to 6.5 cubic centimeters of the latter was heated in a flask supplied with an internal condenser, until there was no further separation of solid from the reddish-brown solution. The product was poured into ice-water, and washed with cold water until the wash-water no longer had an acid reaction. The white, finely crystalline anhydride was purified by recrystallization from alcohol and benzene. After purification, the anhydride was boiled with water, alkalis, and acids. It was found that, while the substance is remarkably stable towards water, it is hydrolyzed by alkalis according to the equation:

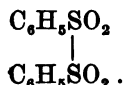


* Ber. d. chem. Ges. 19, 652.

¹⁰ Proc. Chem. Soc., 1892, 42.

There is a marked difference between the behavior of the anhydride and the substance under investigation towards acids. The former, as was to be expected, is readily hydrolyzed by acids, while the latter can be boiled with concentrated hydrochloric acid or crystallized from concentrated nitric acid without undergoing change. In view of these facts the di-sulphone formula must be accepted as the more probable, although it was not possible definitely to disprove the anhydride formula.

II. DIPHENYLDISULPHONE.

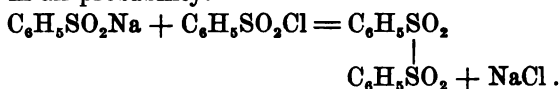


From benzene sulphone chloride and sodium benzene sulphinate.

The sulphinate was prepared by the reduction of the sulphone chloride with zinc dust, and purified by crystallization from water. Benzene sulphone chloride was added to an equivalent quantity of sodium benzene sulphinate in water solution. The mixture was heated to the temperature of a boiling water-bath until there seemed to be no more action. As in the preparation of diparatolyl-disulphone, the substance formed more or less slowly as a white, crystalline, insoluble scum. When the scum no longer increased in amount, the hot solution was filtered. The filtrate contained, besides sodium chloride, some unchanged sulphone chloride, sodium benzene sulphinate, benzene sulphinic acid, and benzene sulphonic acid. The solid was washed with boiling water and ether, and purified by recrystallization from benzene.

All attempts to prepare the diphenyldisulphone in the absence of water, failed. In some preparations the sulphone chloride was dissolved in ether. The yield was not improved by this modification; the reaction, however, proceeded somewhat more rapidly. In no case was the yield more than 20 per cent, nor less than 10 per cent, of the theoretical amount. Other modifications were introduced in the method of preparation with a view to increasing the yield, but without success. No di-sulphone was formed in those experiments in which an excess of sulphone chloride, or of sodium sulphinate was used.

The equation representing the formation of diphenyldisulphone is in all probability:



The formation is, therefore, exactly analogous to that of diparatolyldisulphone. It has also been determined in this case that water is indispensable to the reaction. Thus, a mixture of benzene sulphone chloride and sodium benzene sulphinate in equivalent quantities was heated for several hours without the formation of di-sulphone. Almost immediately on the addition of a few drops of water the di-sulphone began to form.

Like diparatolyldisulphone, diphenyldisulphone is a white, beautifully crystalline substance, insoluble in water and but slightly soluble in ether. It is moderately soluble in chloroform and readily soluble in benzene, from which it crystallizes in small, well defined tables. In order to obtain an absolutely pure substance it is necessary to wash the finely powdered substance many times in hot ether, and recrystallize several times from benzene. The melting point of the pure diphenyldisulphone is 185° - 186° . It melts, unlike diparatolyldisulphone, without decomposition; the melted substance remaining clear with only a very slight brown tint, until the temperature reaches 200° , when the whole becomes black.

An analysis of the substance gave the following results:

I. 0.2198 gram substance gave 0.4050 gram CO_2 .

II. 0.2158 gram substance gave 0.3982 gram CO_2 , and 0.0672 gram H_2O .

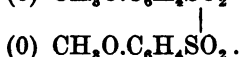
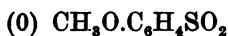
III. 0.2573 gram substance gave 0.4799 gram CO_2 , and 0.0814 gram H_2O .

	Calculated for ($\text{C}_6\text{H}_5\text{SO}_2$) ₂	I.	Found. II.	III.
C	51.06	50.50	50.37	50.83
H	3.54		3.47	3.51

Diphenyldisulphone is more easily decomposed by reagents than diparatolyldisulphone. If boiled with water for several hours it dissolves completely with entire decomposition. Five-tenths of

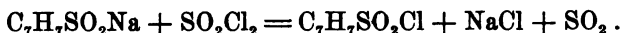
one gram of the substance was boiled for three hours with 15-20 cubic centimeters of water, accomplishing complete decomposition. This solution contained benzene sulphinic acid, identified by its reaction with zinc and acid, and benzene sulphonic acid, identified by its melting point, which was 43°.

III. DIORTHOANISOLDISULPHONE.



This substance was made from ortho-anisolsulphone chloride and sodium ortho-anisolsulphinate.

The sulphinate was made from ortho-anisidine according to the method of Gattermann¹¹ for preparing sulphinic acids. The sulphone chloride was prepared from the sulphinic acid. It had been observed that a sulphone chloride is one of the reaction products when sulphuryl chloride reacts with a sulphinate in the presence of water.



This suggested a method for the preparation of sulphone chlorides, and, in so far as it has been tested, it has proved a very general reaction.

The details of the process are as follows: Sulphuryl chloride was slowly added from a dropping funnel to an ether solution of an equivalent quantity of a sulphinic acid with a constant agitation of the liquid. If enough heat was given off to make the flask feel warm to the hand, it was cooled by holding it in a stream of cold water. This was, however, not always necessary. The addition of a small quantity of water before or after the adding the sulphuryl chloride, was found to be advantageous, but the presence of water is not essential to the reaction. The sulphone chloride crystallized from the ether solution, on evaporation, in a comparatively pure condition. The quality of the product was much improved by shaking the ether solution with an equal volume of water, and separating the two solutions after half an

¹¹ Ber. d. chem. Ges., **32**, 1141.

hour's standing. The water solution was acid and possessed a strong odor of sulphur dioxide. The reaction involved in the formation of the sulphone chloride may be represented by the equation:



The yield of sulphone chloride was in every instance good. Ten grams ortho-anisolsulphinic acid gave 10.5 grams sulphone chloride after one recrystallization from ether. In this preparation the crude product melted at 55°-57°, after one recrystallization from ether it melted at 55°. The correct melting point of ortho-anisolsulphone chloride is 55°.

The applicability of this method was tested in the preparation of para-tolylsulphone chloride, ortho-anisolsulphone chloride, α , naphthalenesulphone chloride, and meta-xylenesulphone chloride, with equally good results in all cases. Since Gattermann's method for preparing sulphinic acids may be so generally and successfully employed, the above method for making sulphone chlorides of definite structure will be found most convenient.

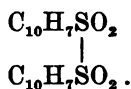
Diorthoanisoldisulphone was prepared by the continued heating of a mixture of equivalent quantities of ortho-anisolsulphone chloride in ether solution, and sodium ortho-anisolsulphinate in water solution. The substance is, in appearance, much like the two di-sulphones already described. It separates as it is formed in much the same way. It crystallizes well from benzene, which is the best solvent for it. Its one impurity, sulphone chloride, was removed with some difficulty, by repeated washings with ether and recrystallization from benzene. The melting point obtained for diorthoanisoldisulphone was 184°-185° with decomposition. The yield was small, averaging about 10 per cent. All attempts to increase the yield by modifying the conditions were unsuccessful.

An analysis of the substance gave the following results:

I. 0.1010 gram substance gave 0.1806 gram CO_2 , and 0.0360 gram H_2O .

	Calculated for ($\text{CH}_3\text{OC}_6\text{H}_4\text{SO}_2$) ₂	Found. I.
C	49.12	48.71
H	4.09	3.96

IV. DI-NAPHTHALENEDISULPHONE.



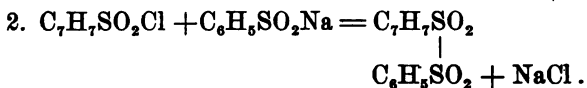
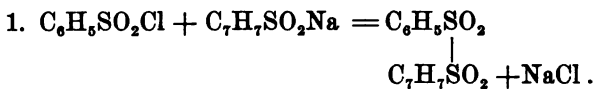
The sulphone was made from α -naphthalene sulphone chloride and sodium α -naphthalene sulphinat.

The sulphinic acid was prepared according to the Gattermann method, and the sulphone chloride from the acid by treatment with sulphuryl chloride according to the method already described under diorthoanisoldisulphone. A mixture of equivalent quantities of ortho-anisolsulphone chloride in ether solution, and sodium ortho-anisolsulphinate in water solution, was heated until there was no longer any reaction. The substance separated out as described in the preparation of other di-sulphones. It closely resembles them in appearance, being, however, slightly colored, but less so than ortho-anisolsulphinic acid, which has a decidedly yellow tint. Although soluble in benzene, it does not crystallize well from this solvent. The substance also readily dissolves in nitrobenzene, and is partially deposited from its solution in this solvent as a crystalline powder. The melting point of the crystals from benzene solution was found to be 184° - 186° , with decomposition.

V. PHENYL-PARATOLYLDISULPHONE.

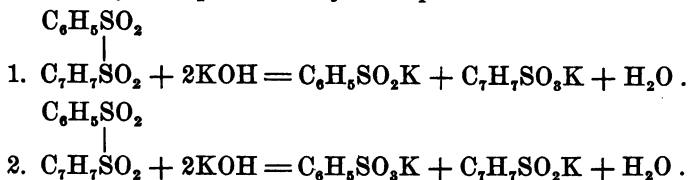


This was prepared from benzenesulphone chloride and sodium para-tolylsulphinate, and also from para-tolylsulphone chloride and sodium benzenesulphinate.

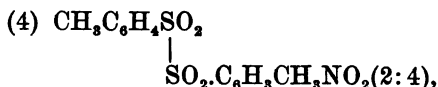


The substance is a white solid very similar to diparatolydi-

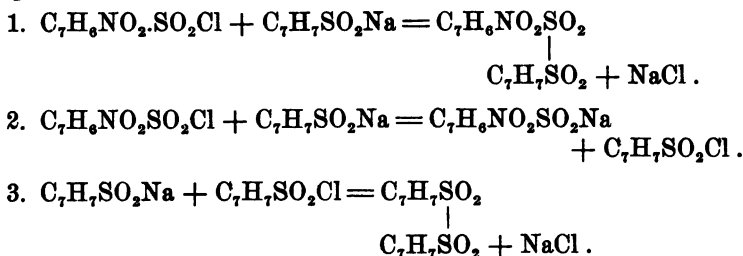
sulphone in crystalline form, but dissolves more easily in ether and benzene, and is readily soluble in chloroform. Its melting point is 166°. Phenylparatolyldisulphone is decomposed by boiling caustic potash. Potassium chloride, potassium benzenesulphonate, potassium benzenesulphinate, potassium tolylsulphinate, and potassium tolylsulphonate were found in the diluted solution. Its decomposition may be represented by the equations:



VI. PARATOLYLPARANITROORTHOTOLYLDISULPHONE.



was prepared from sodium para-tolylsulphinate and paranitro-orthotolylsulphone chloride. In the preparation of this substance, by heating an ether solution of the sulphone chloride and a water solution of the sodium sulphinate, mixed in equivalent amounts, diparatolyldisulphone was also formed. This would indicate a secondary reaction between the sulphone chloride and the sulphinate similar to the reaction between sulphuryl chloride and sulphinic acid.



The two substances being almost equally soluble, crystallized together from benzene, the paratolymparanitroorthotolyldisulphone in thick, slightly colored prisms. This difference in the appear-

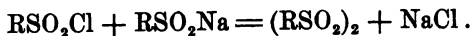
ance of the two substances made it possible to separate the two kinds of crystals, and by fractional crystallization from chloroform the paratolylparanitroortholydisulphone was obtained in a pure condition. It melts at 154° .

No combustions of the last three substances were made because of the limited amount of material. There is, however, sufficient reason for believing they were obtained in a pure condition, and that the melting points are correct.

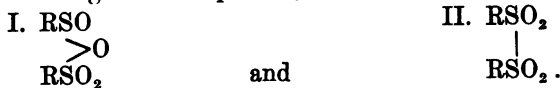
CONCLUSION.

The experiments described above show that 1, 2 di-sulphones, while difficult to make, are capable of existence, and, therefore, that it is possible to get organic sulphur compounds that contain two hexavalent sulphur atoms in direct union. The evidence on which this statement is based is as follows:

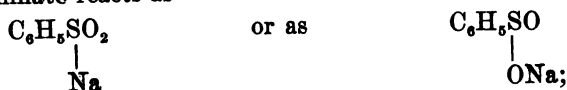
By the reaction between sulphone chlorides and sulphinates substances are formed whose composition and molecular weight are represented by the general formula $(\text{RSO}_2)_2$. The reaction by which these substances are formed must, therefore, be represented by the equation:



There are but two possible structural formulas for a substance formed according to this equation,



The method of preparation does not supply any basis on which to decide between these formulas because it is not known whether the sulphinate reacts as



and the matter is complicated by the fact that the reaction takes place only in the presence of water.

Formula I represents a mixed anhydride of a sulphonic and a sulphinic acid. Anhydrides of sulphonic acids and mixed anhy-

drides of sulphonic acids and carbonic acids are known. These are all readily hydrolyzed by acids and alkalis. Quite the opposite of this is the case with the substances under consideration. Acids apparently do not hydrolyze them at all. When heated with concentrated hydrochloric acid in sealed tubes they are ultimately decomposed, but the process is not hydrolysis. When boiled with alkalis, they are decomposed into sulphinates and sulphonates. The process is one of hydrolysis:

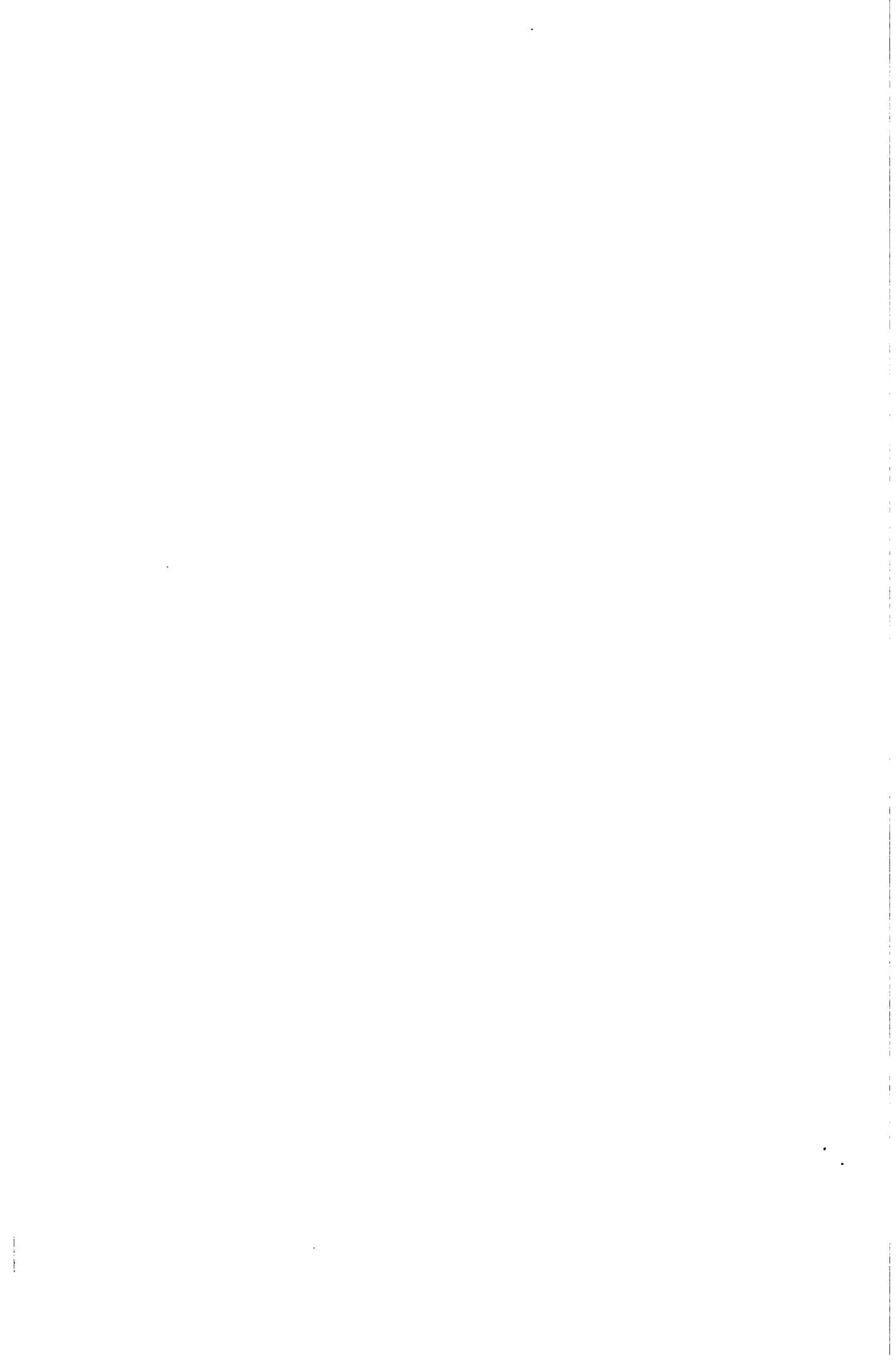


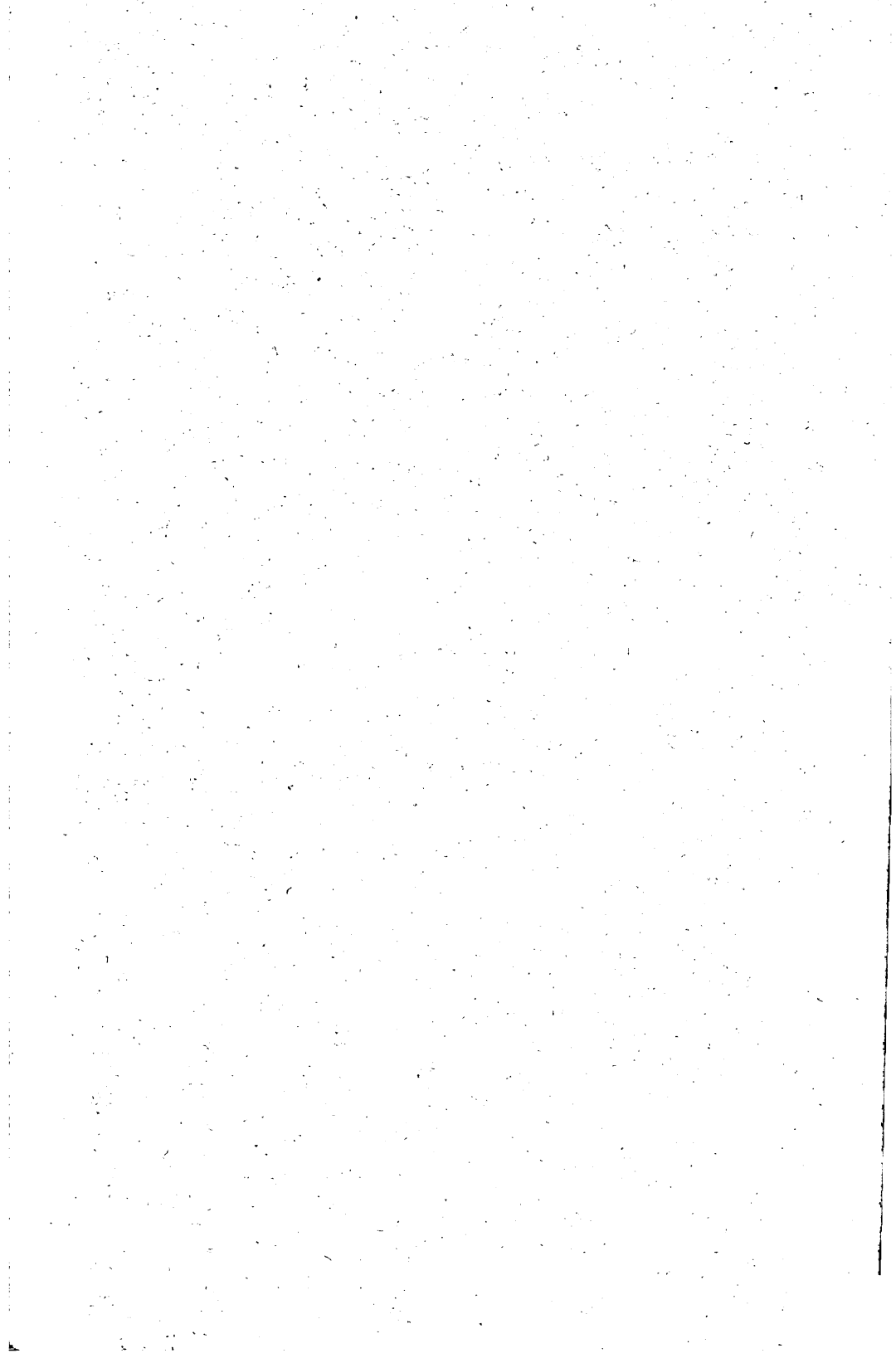
but takes place with much greater difficulty than would be expected in any anhydride containing a sulphonic acid residue.

Formula I also represents a substance containing a sulphinic acid residue. All known sulphinic acids are easily oxidized. It would be expected, therefore, that a substance with this formula would behave in the same way. The substances under consideration, however, are extremely stable in the presence of oxidizing agents. Potassium permanganate has no action on them, and they can be crystallized from concentrated nitric acid without loss. Formula I does not agree with the properties of the substances.

Formula II represents a di-sulphone. Sulphones, as a class, are marked by great crystallizing power, insolubility in water, high melting and boiling points, stability and inertness. The substances under consideration crystallize in hard, lustrous, perfectly-formed crystals; they are insoluble in water, difficultly soluble in organic solvents; they all melt at a high temperature—most of them with decomposition; they are stable, and, as has been shown, unusually inert. The properties of these substances, therefore, agree with the requirements of formula II; the substances are 1, 2 di-sulphones.

As a result of this investigation a new class of di-sulphones, containing hexavalent sulphur, has been discovered. Several members of the class have been isolated; their properties, both physical and chemical, have been noted; the reactions involved in their formation have been studied; and their constitution has been determined. While too inert to take part in chemical transformations, the 1, 2 di-sulphones are of theoretical importance, since they constitute the missing class in the series of di-sulphones.





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- I. The Addition Reactions of Sulphinic Acids. By MARIE REIMER.
- II. A New Class of Disulphones. By MARGARET BAXTER MACDONALD.

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